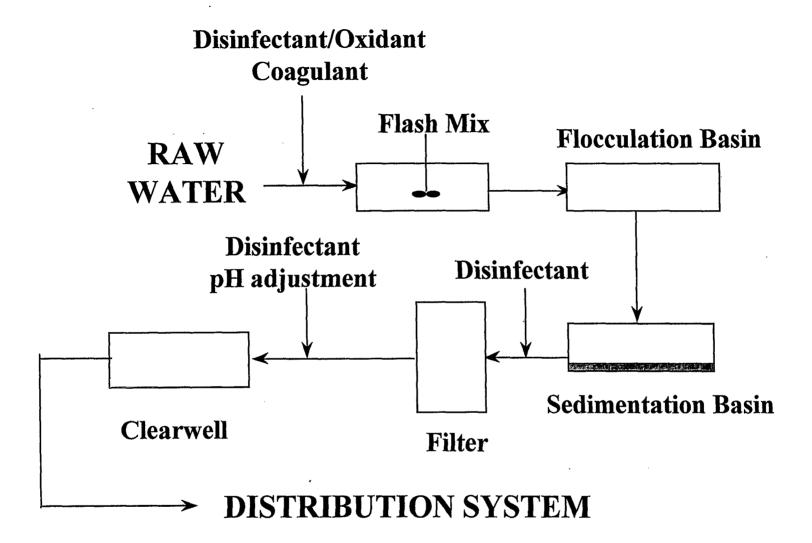
## Treatment of Delta Waters

Stuart W. Krasner
Metropolitan Water District
of Southern California

#### Treatment of Delta Waters

- What are the impacts of using different treatment methods on Delta water?
- What are the current and future regulations?
  - Disinfection By-Product (DBP) Rule
  - Enhanced Surface Water Treatment Rule (ESWTR)
- Can future regulations be met?

# Current Treatment/ Disinfection Practices

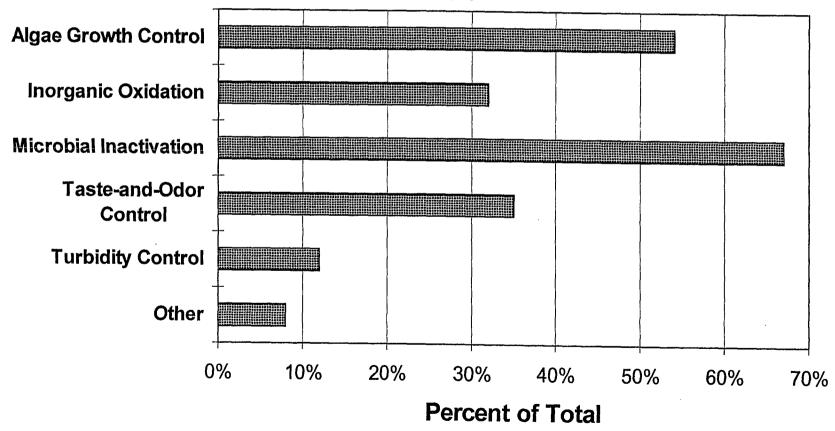


# **Typical Conventional Water Treatment Plant Schematic**

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Drinking water systems use predisinfection/preoxidation to control a variety of water quality problems (e.g., iron and manganese, sulfides, zebra mussels, Asiatic clams, taste and odor).

1997 Survey of 329 Large Surface Water Treatment Plants: (Multiple) Reason(s) for Predisinfection

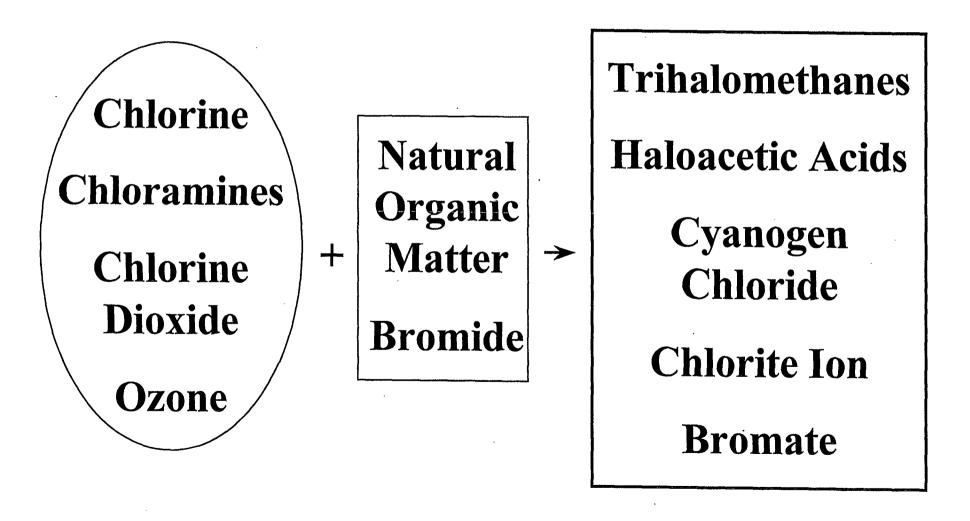


#### Disinfectants Used in Drinking Water

- Chlorine: Proven effectiveness, low capital and operating costs, extensive experience
- Chloramines: Compared to chlorine (1) produces less DBPs, (2) residual is longer lasting, (3) less effective microbial inactivation
- Chlorine dioxide: Effective disinfectant and oxidant, does not form trihalomethanes, principal by-product is chlorite ion
- Ozone: Highly reactive, very effective disinfectant and oxidant, produces oxidation by-products

# Chemistry of DBP Formation

# Disinfectant + Precursor ---> DBPs (impacted by water quality parameters)

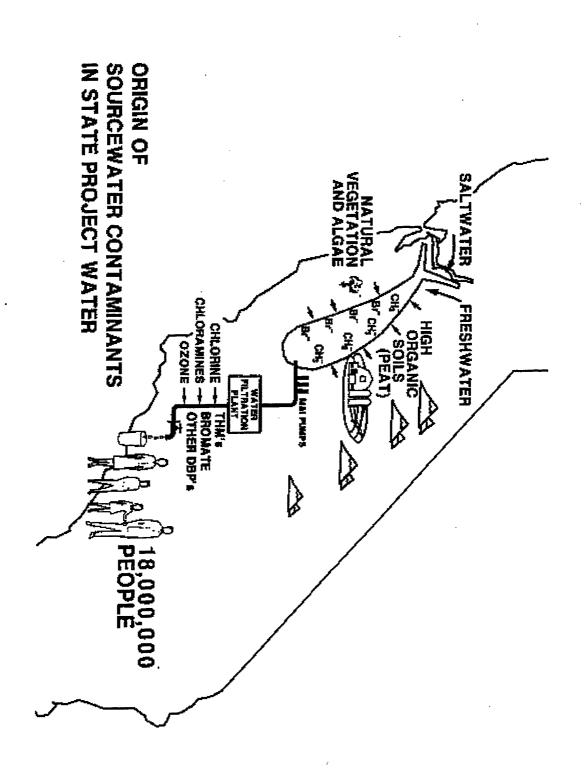


#### Natural Organic Matter

- Sources: Decaying vegetation, peat soil, algae, etc.
- Surrogate parameter: Total organic carbon (TOC) measure of amount of natural organic matter in water

#### **Bromide**

- Saltwater intrusion
- Geologically-trapped ancient seawater
- Oil-field brines

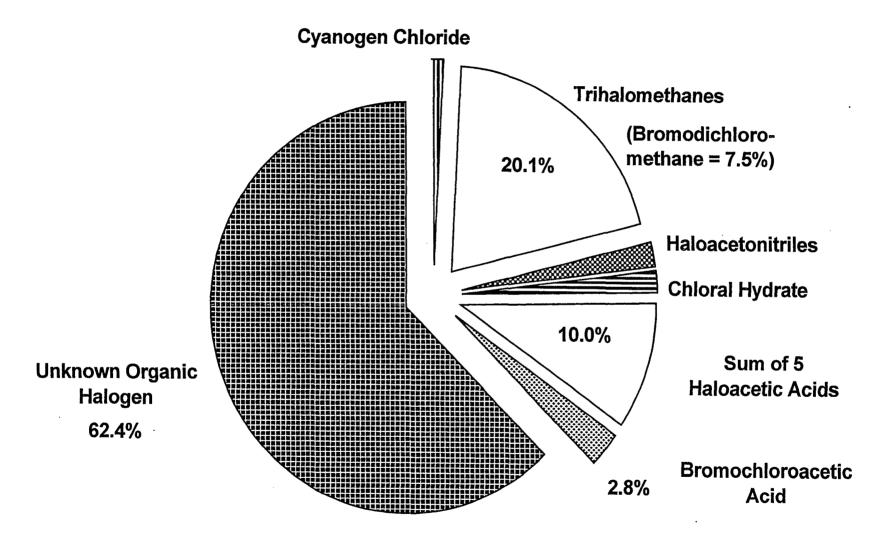


Generalized conceptual model for the formation of major organic halide products from fulvic acid (a portion of the natural organic matter) (adapted from Reckhow and Singer, 1985)

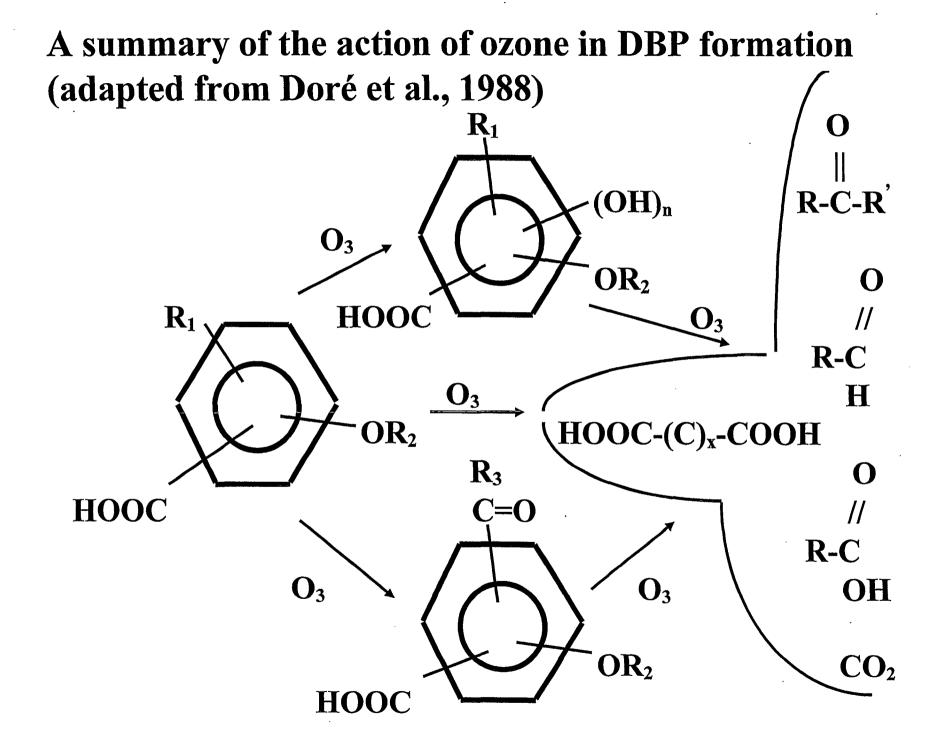
FULVIC ACID  $\rightarrow$  R'-CO-CH<sub>2</sub>-CO-R  $\rightarrow$  R'-CO-CCl<sub>2</sub>-CO-R CHCl<sub>2</sub>COOH CCl<sub>3</sub>-CO-CH<sub>3</sub> → CHCl<sub>2</sub>-CO-R  $R = CH_2$ CCl<sub>3</sub>-CO-CHCl<sub>2</sub> CCl<sub>3</sub>-CO-R pH 12 pH 7  $R \neq OFG^*$  $R = OFG^*$ CHCl<sub>3</sub> CCl<sub>3</sub>COOH

\*Where OFG = oxidizable functional group

# Percentage of Total Organic Halogen Accounted for by DBPs in Information Collection Rule (on a Molar Basis)\*



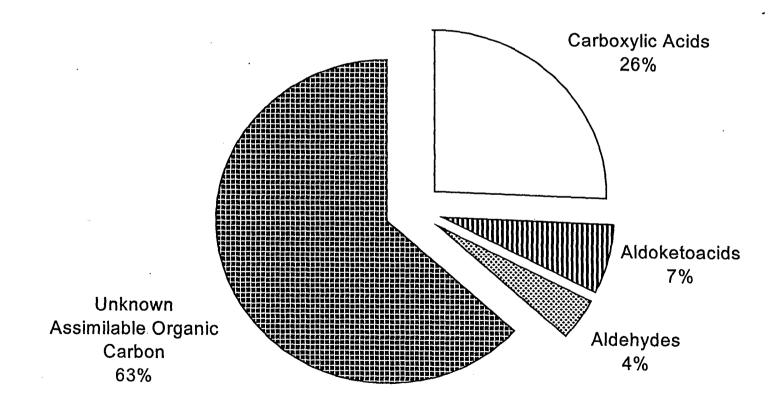
<sup>\*</sup>Mills Plant (CA) finished water, August 1997 (Total organic halogen = 172 µg/L, raw-water bromide = 0.15 mg/L)



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# Formation of Biodegradable Organic Matter (TOC = 2.2 mg/L, biodegradable organic carbon = 0.5 mg/L)

Relative Composition of Assimilable Organic Carbon (286  $\mu$ g C/L) in Filter Influent (Krasner et al., 1996) [Assimilable Organic Carbon in Filter Effluent = 104-129  $\mu$ g C/L]



# Regulatory Background

# Stage 1 DBP Rule

- Promulgated December 1998
  - Lowered maximum contaminant level (MCL) for trihalomethanes to  $80 \mu g/L$
  - Established MCL for sum of 5 haloacetic acids at  $60 \,\mu g/L$
  - Established MCLs for bromate at 10  $\mu g/L$  and for chlorite at 1 mg/L
  - Also requires removal of DBP precursors (i.e., TOC)

### Required Removal of TOC by Enhanced Coagulation for Surface-Water Systems Using Conventional Treatment

Alkalinity, mg/L as CaCO<sub>3</sub>

TOC (mg/L)	0-60	>60 - 120	>120
>2.0 – 4.0	35.0	25.0	15.0
>4.0 – 8.0	45.0	35.0	25.0
>8.0	50.0	40.0	30.0

# Stage 2 DBP Rule

- Will be promulgated by May 2002
  - Currently being negotiated
  - Placeholder MCLs in 1994 proposed rule
    - 40 μg/L for trihalomethanes
    - 30 μg/L for haloacetic acids
    - 5 μg/L for bromate
  - To be promulgated with ESWTR
    - May include inactivation requirement for *Cryptosporidium*

# Other Stage 2 DBP Rule Options

- Set MCLs for individual DBPs of health concern
  - Certain brominated DBPs (e.g., bromodichloromethane) (1) have higher cancer potencies and (2) have been associated with adverse reproductive/developmental health effects (e.g., spontaneous abortion)
- Eliminate aspects of the current compliance formula based on a running annual average

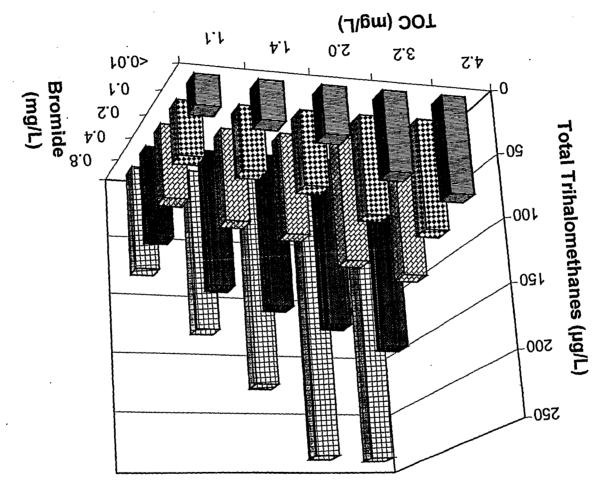
# Effect of TOC (NOM) and Bromide on DBP Formation

# Effects of TOC (NOM) and Bromide on DBP Formation (Krasner et al., 1994; Najm & Krasner, 1995)

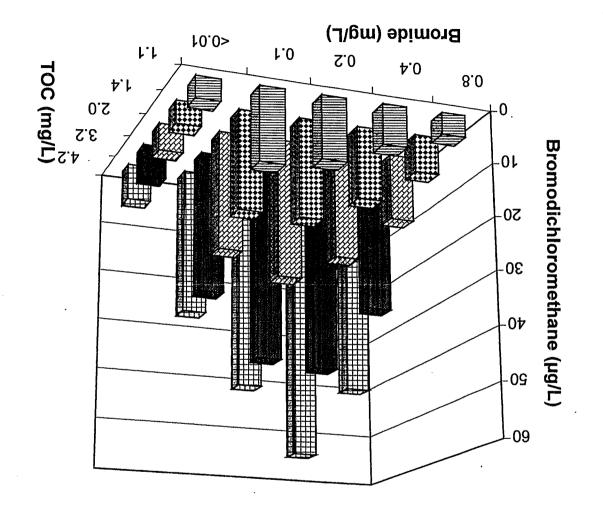
- Experimental approach
  - "Baseline" water = Sacramento River water upstream of the Delta
    - TOC = 1.1-1.2 mg/L, bromide < 0.01 mg/L
  - Water spiked with 5 levels each of TOC and bromide (5 x 5 matrix: 25 unique waters)
    - TOC spike = agricultural drain (35 mg/L TOC)
    - TOC evaluated = 1.1 to 4.2 mg/L
    - Bromide evaluated = <0.01 to 0.8 mg/L

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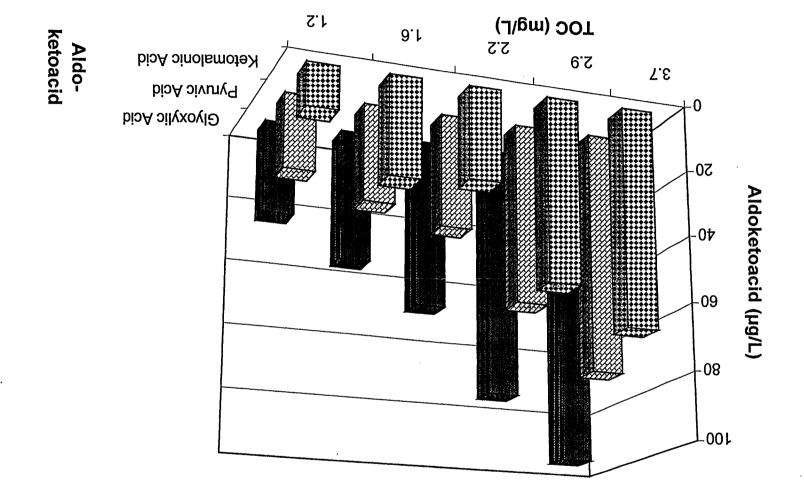
Effect of TOC and Bromide on the Formation of Total Trihalomethanes: Temperature = 25 C, pH = 8.2, Reaction Time = 3 hr (Krasner et al., 1994)



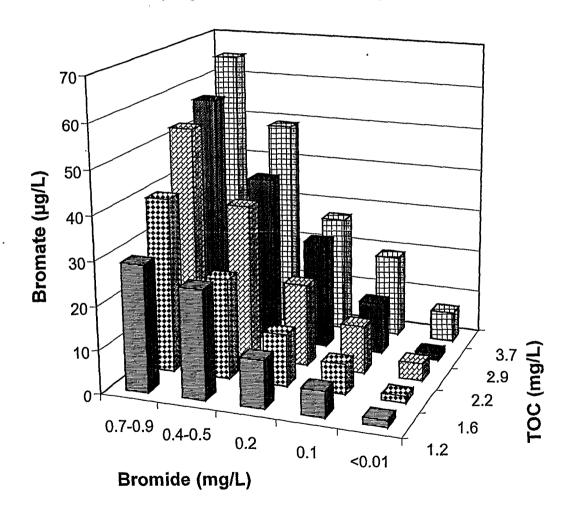
Effect of TOC and Bromide on the Formation of Bromodichloromethane: Temperature = 25 C, pH = 8.2, Reaction Time = 3 hr (Krasner et al., 1994)



Effect of TOC on Aldoketoacid Formation (Average of 5 Bromide Tests): Ozone/TOC = 2.1 mg/mg; Ozone Residual = 0.35 mg/L (Najm & Krasner, 1995)



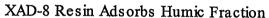
# Effect of TOC and Bromide on Bromate Formation: Ozone/TOC = 2.1 mg/mg; Ozone Residual = 0.35 mg/L (Najm & Krasner, 1995)

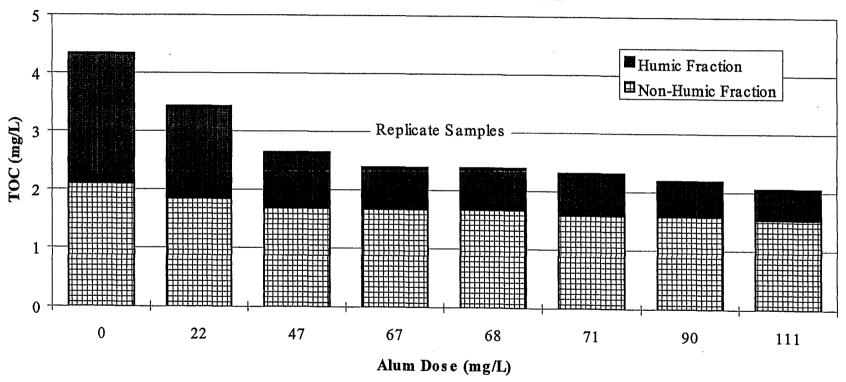


# Effect of Using Different Treatment Methods on Delta Water

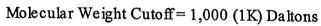
Effect on TOC (NOM)

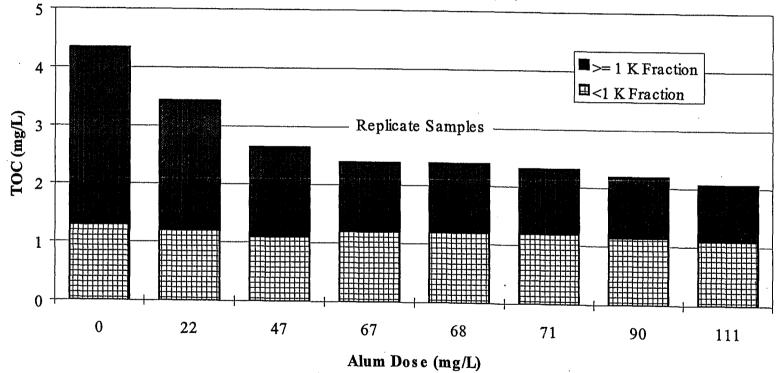
#### Enhanced Coagulation of State Project Water (Krasner et al., 1994)





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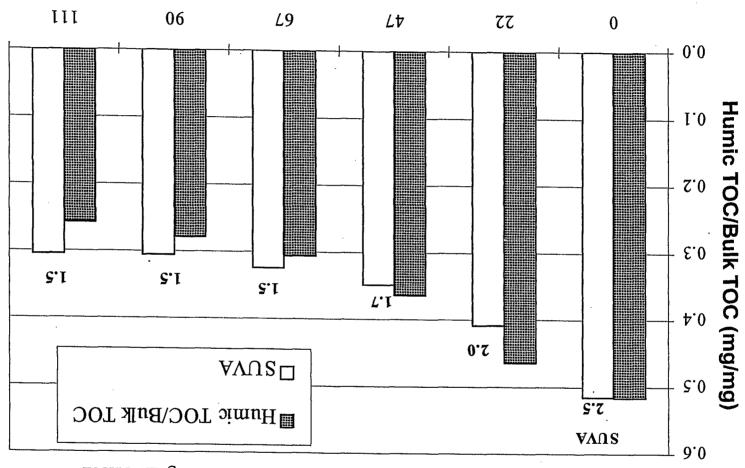




# D-0360

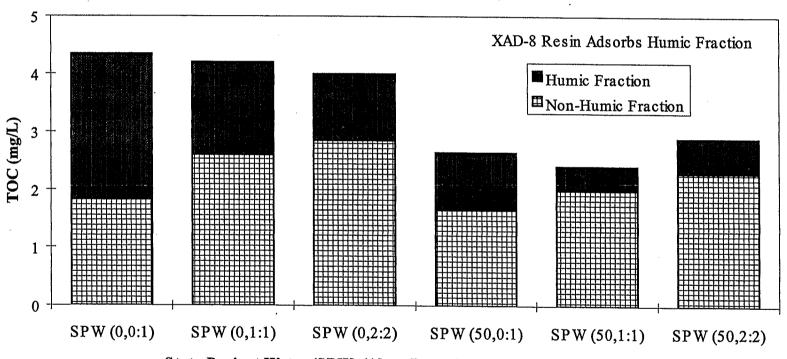
# Enhanced Coagulation of State Project Water (Krasner et al., 1994)

SUVA = Specific Ultraviolet Absorbance = UV \* 100/Dissolved Organic Carbon



Alum Dose (mg/L)

# Enhanced Coagulation and Ozonation of State Project Water (Krasner et al., 1994)

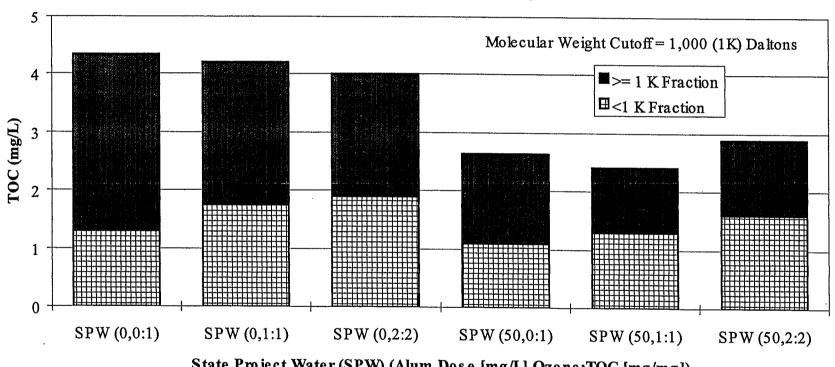


State Project Water (SPW) (Alum Dose [mg/L], Ozone:TOC [mg/mg])

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#### Enhanced Coagulation and Ozonation of State Project Water (Kras ner et al., 1994)



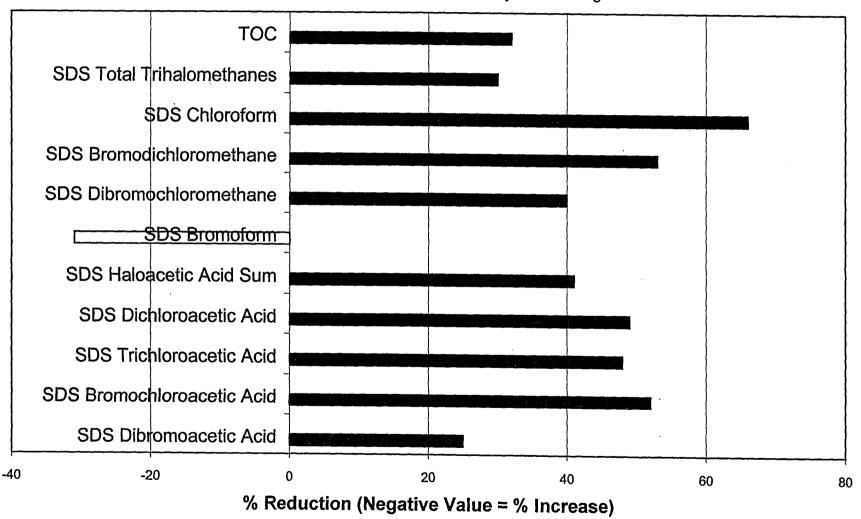
State Project Water (SPW) (Alum Dose [mg/L],Ozone:TOC [mg/mg])

# Effect of Using Different Treatment Methods on Delta Water

Effect on DBPs

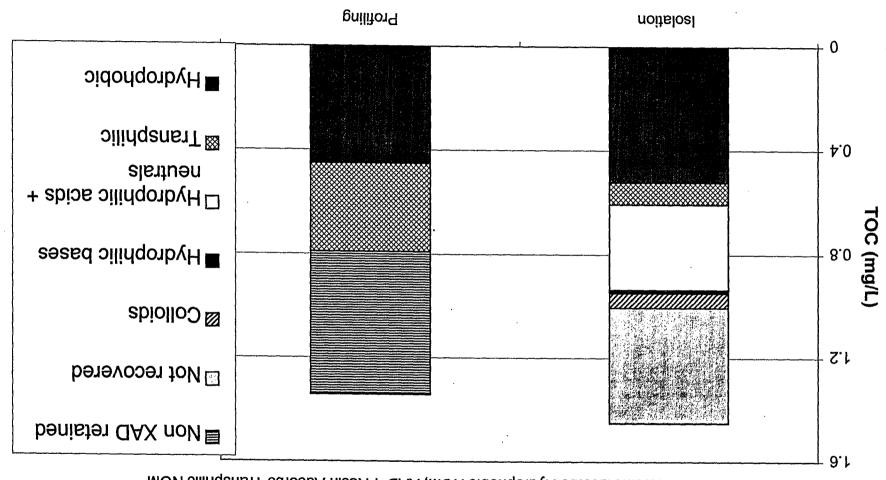
#### Enhanced Coagulation of State Project Water (Cheng et al., 1995): Coagulation Removes TOC, But Not Bromide

SDS = Simulated Distribution System Testing



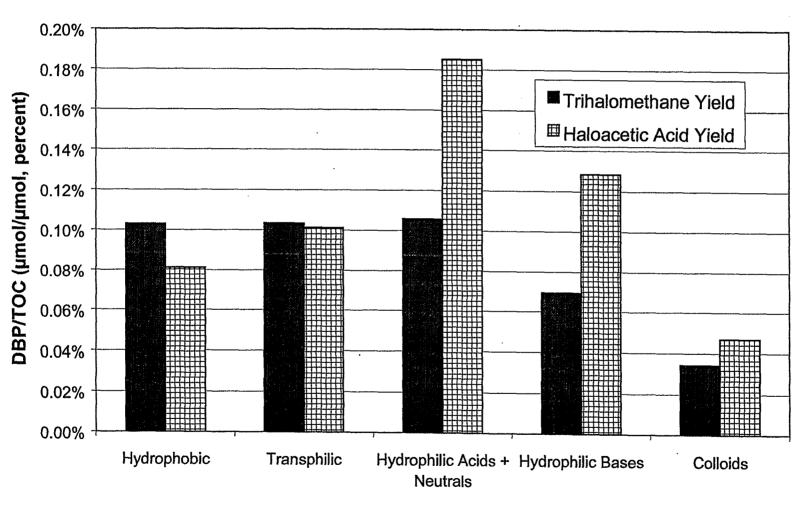
# TOC Distribution of Delta Water at City of Martinez: Ozone Contactor 2 Effluent

XAD-8 Resin Adsorbs Hydrophobic NOM, XAD-4 Resin Adsorbs Transphilic NOM



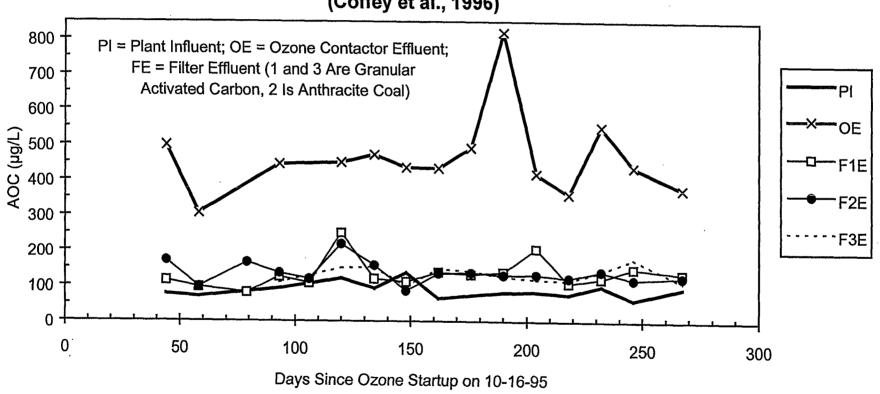
Method of NOM Characterization

#### DBP Yields for Delta Water at City of Martinez: Ozone Contactor 2 Effluent NOM Isolates



**NOM** Isolate

# Production and Removal of Assimilable Organic Carbon (AOC) During Ozonation/Biofiltration of State Project Water (TOC ~3 mg/L) (Coffey et al., 1996)



# Can Future Regulations Be Met?

Stage 2 (Stage 3) DBP Rule?

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# Can Future Regulations Be Met?

- Expert panel: Need TOC of 3 mg/L and bromide of 50 μg/L (0.05 mg/L)
- Need to meet these goals at all times of year if compliance with DBP MCLs no longer allows for running annual averages
- California Department of Health Services even considered eliminating certain aspects of the running annual average for Stage 1